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## EUROPEAN PATENT APPLICATION

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• **Dennis, Paul Vincent**  
**Nr. Daventry, Northants NN1 3SR (GB)**

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(74) Representative: **Walker, Andrew John**  
**The General Electric Company plc**  
**Patent Department**  
**Waterhouse Lane**  
**Chelmsford, Essex CM1 2QX (GB)**

(71) Applicant: **GEC MARCONI LTD.**  
**Stanmore, Middlesex HA7 4LY (GB)**

(72) Inventors:  
• **Reece, David Michael**  
**Northampton, Northants NN1 4HZ (GB)**

### (54) Coatings

(57) A scratch resistant coating (44) for the window (42) of an infra red sensor comprises a layer of zirconium oxynitride or hafnium oxynitride. The formula of the

coating is  $M_{1-(y+z)}O_yN_z$  where y and z are both in the range 0.1 to 0.4. The coating (44) and the window (42) are both transmissive in the infra red and visible ranges of the spectrum.

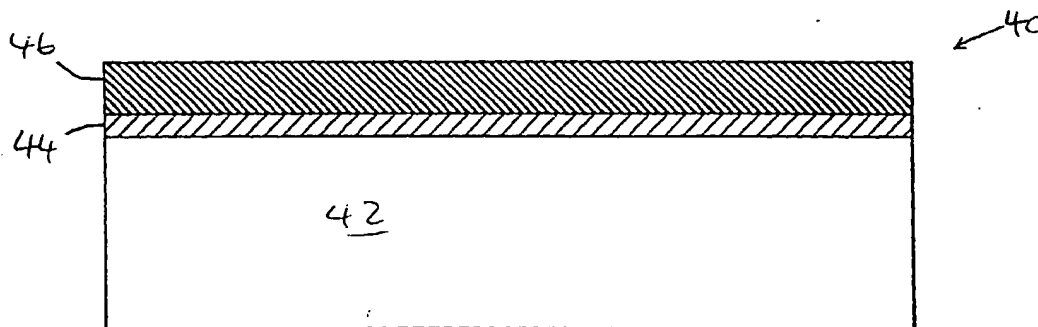


FIGURE 4.

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## Description

This invention relates to coatings for infra-red transparent materials and applies particularly, but not exclusively, to coatings for multispectral window materials.

Infra-red (IR) radiation means radiation which is in the wavelength range in the region of approximately 1 $\mu$ m to approximately 14 $\mu$ m. This includes a first IR radiation range of 3 $\mu$ m to 5 $\mu$ m and a second IR radiation range of 8 to 14 $\mu$ m. Radiation in the range 5 $\mu$ m to 8 $\mu$ m is largely absorbed by the atmosphere. Measured IR radiation can be used to determine a value of temperature of a body or to observe objects particularly when visible light levels are low.

IR detectors are usually relatively fragile and need to be protected from their environment, for example atmospheric conditions and physical contact. Therefore they are placed behind windows or domes which are made of materials transparent to the radiation that is being detected. Since many IR window materials are inherently soft and have poor scratch resistance, they suffer from erosion. Airborne systems suffer from rain, sand and insect damage inflicted at high velocities. In land based systems a combination of sand and window wipers can cause scratches.

It is known to protect IR windows by coating them with a hard protective coating. Known protective coatings for IR windows include diamond-like carbon (which is disclosed in British Patent GB 2082562 B) and boron phosphide (which is disclosed in British Patent GB 2223510 B).

However, a disadvantage of the use of such coatings is that they do not transmit radiation at visible wavelengths. The term visible refers to wavelengths approximately between 300nm and 1000nm (1 $\mu$ m). Since sensor systems may comprise detectors to detect visible radiation in addition to IR and it is convenient to locate both kinds of detector behind the same window, a hard multi-wavelength coating material is needed.

According to a first aspect the invention provides a coating material for a window the coating material comprising metal oxynitride and being substantially transmissive to visible radiation and to IR radiation.

It is to be understood that the term transmissive means capable of transmitting a useful amount of incident radiation. Preferably the transmissivity of a coating of the coating material is 50% for a coating which is about 100 $\mu$ m thick, more preferably about 50 $\mu$ m thick and most preferably about 10 $\mu$ m thick. Preferably the metal oxynitride transmits substantially across the range 1  $\mu$ m to 14 $\mu$ m. Most preferably the metal oxynitride transmits in the range 8 $\mu$ m to 14 $\mu$ m.

The window may be a window for a sensor. The term sensor refers to one or more electronic devices for detecting or emitting electromagnetic radiation in the ranges of IR, visible or both.

The chemical formula of the coating material is  $M_{1-(y+z)}O_yN_z$  where M represents a metal element or

combination of metals and with y and z having values which vary depending upon the desired properties of the coating material. Preferably y is in the range 0.1 to 0.4. Preferably z is in the range 0.1 to 0.4. The values of y and z can vary depending on the metal or combination of metals used. For example, for zirconium y is approximately 0.35 and z is approximately 0.20, whereas for hafnium, y is approximately 0.17 and z is approximately 0.33. Preferably the metal is one or more metals from the transitions and lanthanide metal series. Most preferably it is zirconium or hafnium or a combination of both.

The window may comprise any of the following materials: zinc sulphide, zinc selenide, germanium, silicon, quartz or sapphire. Alternatively the window may be comprised substantially wholly of the metal oxynitride, such that the metal oxynitride is self supporting.

Preferably the coating is of a thickness between 5 $\mu$ m and 15 $\mu$ m although coatings of greater thickness, up to 50 $\mu$ m may be manufactured.

The metal oxynitride material may be formed by ion beam sputtering. Preferably dual ion beam sputtering is used. Most preferably reactive dual ion beam sputtering is used. Preferably the sputtering target comprises metallic zirconium, hafnium or both. Alternatively compounds of zirconium or hafnium may be used as the target.

The metal oxynitride may coat one or on both sides of the window.

The metal oxynitride may be the outermost coating on the window, that is the coating exposed to the atmosphere. Alternatively the metal oxynitride may comprise a bonding layer between the window and another coating, such as a hard outer coating or an anti-reflection coating. Such a bonding layer may be between 0.01 $\mu$ m and 1.0 $\mu$ m thick although in some applications it may be thicker, for example, of the order of 20  $\mu$ m. The metal oxynitride coating may comprise a protective interlayer for protecting the window material from further coatings to be applied to the window. An interlayer may also provide stress relief between coatings adjacent to it.

Advantageously one or more metal oxynitride coatings comprise both bonding layers and protective interlayer layers.

According to a second aspect the invention provides a method of producing a coating of metal oxynitride on a sensor window comprising the steps of:

- providing a sputtering target containing the metal in vacuum chamber;
- sputtering the target with a primary ion gun ;
- bombarding the substrate with ions of oxygen, nitrogen or both from a secondary ion gun; and
- depositing a coating of metal oxynitride on the substrate.

The invention may also provide a metal oxynitride coating made in accordance with the second aspect of

the invention.

Preferably the substrate is maintained at a temperature in the range 100 to 500°C, most preferably in the range 300 to 400°C. The target may comprise metallic hafnium, zirconium, or a combination of these metals such as an alloy. Alternatively the target may comprise hafnium nitride, zirconium nitride, hafnium oxide or zirconium oxide.

The metal oxynitride may be of the formula  $M_{1-(y+z)}O_yN_z$ . The final composition of the coating material, that is the values of y and z, may be controlled by controlling the amount of oxygen, nitrogen or both which is fed to the secondary gun or by the composition of the target material which may be a nitride, oxide or oxynitride of the oxynitride coating material to be formed.

According to a third aspect the invention provides a window coated with a coating in accordance with the first or second aspects of the invention.

According to a fourth aspect the invention provides a radiation source and/or detector system comprising a window in accordance with the third aspect of the invention.

Preferably the system comprises one or more devices for detecting electromagnetic radiation in the ranges of IR, visible or both. Preferably the system comprises one or more sources of electromagnetic radiation in the ranges of IR, visible or both. The sensor system may comprise devices which are radiation sources such as lasers.

An embodiment of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 shows a sputtering system;

Figure 2 shows a graph of transmission of a coated IR window material across visible wavelengths;

Figure 3 shows a graph of transmission of a coated IR window material across infra-red wavelengths; and

Figure 4 shows a schematic representation of a coated IR window.

Figure 1 shows a sputtering system 2 known in the art as a dual ion beam system (DIBS). The system 2 comprises a vacuum chamber 4 which is evacuated by a turbomolecular pump (outlet 6) and a cryopump (outlet 8). A target 10 is located in the vacuum chamber 4 together with a substrate 12 which is supported on a substrate holder 14. The target 10 is angled towards the substrate.

The target is comprised of zirconium or hafnium metal although nitrides or oxides of these metals may be used.

Two ion beam guns operating at radio frequency are in the vacuum chamber. A primary ion beam gun 16 which is fed by a supply 18 of inert gas, for example argon or krypton, produces a focussed primary ion beam 20 which is directed towards the target 10. A sec-

ondary ion beam gun 22 produces a diffuse secondary ion beam 24 which is directed towards the substrate 12. The secondary ion beam gun 22 is fed by a gaseous supply 26 of oxygen and nitrogen.

The substrate holder 14 is rotatable about an axis 28 in order to control the uniformity of deposition of material on the substrate. The substrate holder is also tilt-able through an arc 30 of 0 to 45° for controlling the composition of the materials deposited. The substrate holder also comprises heating means (not shown) to heat the substrate to a temperature suitable for deposition. A two colour IR pyrometer 32 is used to measure the temperature of the substrate.

In operation the primary ion beam gun 16 is supplied with krypton gas which is ionised and fired at the target 10 as a focussed beam. Impact of krypton ions on the target sputters target material out of the target. Sputtered target material which lands on the substrate forms a coat on the substrate. The substrate may be rotated during sputtering. The temperature of the substrate is controlled by heating means. During coating the substrate is held at a temperature of about 350°C.

As target material is being sputtered onto the substrate the secondary ion beam gun 22 directs ions towards the substrate. Oxygen and nitrogen ions are used to bombard the substrate if a metallic target is used. For example if a target of zirconium metal is used, oxygen and nitrogen ions are fired from the gun 22 simultaneously or alternately in order to form zirconium oxynitride. If the target were to be zirconium nitride an oxygen ion beam with little or no nitrogen ion content would be used. The converse would apply if a zirconium oxide target was used. Therefore a coating of zirconium oxynitride can be built up on the substrate. A target comprising hafnium could be used to manufacture a coating of hafnium oxynitride.

An example of a fabrication method to make a zirconium oxynitride coating using a Nordiko 3450 dual ion beam sputtering system set to the following parameters:

Parameter	zirconium oxynitride
Pan angle	73°
Chamber pressure	$1.3 \times 10^{-4}$ torr
Deposition temperature	330-350 °C
Gun 1 Krypton flow	20sccm
Gun 1 Voltage	700V
Gun 1 Current	90mA
Gun 2 Nitrogen flow	35sccm
Gun 2 Oxygen flow	5sccm
Gun 2 Voltage	100V
Gun 2 Current	40mA

A hafnium oxynitride coating may be made using the same parameters if an appropriate target material is used, for example a hafnium metal target.

Prior to deposition of the coating the substrate may

be cleaned by using an inert gas ion beam from the secondary ion gun.

Using this method metal oxynitride coatings having been deposited on such substrate materials as germanium, zinc sulphide, silicon and fused quartz. The coatings are in the region of 10µm thick. Using the metal oxynitride coatings is desirable because they are hard and scratch resistant. However, unlike coatings which have been known hitherto these metal oxynitride coatings have good transmission properties across both visible and IR wavelengths.

The transmission in the visible part of the spectrum through a 1.5 µm thick zirconium oxynitride film deposited on a fused silicon substrate is shown in Figure 2. As shown in the graph the transmission is around 50% in the visible region. Some of the incident light which is not transmitted is due to reflection from the coating surface and the coating/substrate interface. It is anticipated that transmission values of up to 99% may be obtained should the zirconium oxynitride coating be coated with an anti-reflection coating.

The transmission in the IR part of the spectrum between 8 µm and 12µm through a 7µm thick zirconium oxynitride film deposited on a germanium substrate is shown in Figure 3. As shown in the graph the transmission is around 50% in the infra red region. Again much higher transmission values are anticipated should anti-reflection coatings be used.

In order to achieve adequate adhesion of a metal oxynitride coating to some substrates a thin bonding layer may be used as a layer between the substrate and the coating. The bonding layer may be deposited on the substrate by the dual ion beam method or some other suitable method prior to deposition of the metal oxynitride coating using appropriate materials and coating techniques. The bonding layer may comprise one or more of the following: germanium, germanium nitride, silicon, hafnium or zirconium oxide or nitride. However any layer which will bond to the window and to an outer coating and when sufficiently thin will transmit visible and infra red radiation may be used. The layer would be approximately 0.1 µm thick. Alternatively a layer of zirconium oxynitride or hafnium oxynitride may itself form a bonding layer on which another coating, for example an anti-reflection coating, is deposited.

In some applications IR windows may be coated with a diamond coating. This provides high erosion and impact resistance due to the exceptional hardness of diamond. Furthermore, since diamond can transmit radiation in both visible and infra red wavelengths it has excellent transmission properties for use as a coating in this type of application.

A suitable method of applying a diamond coating is plasma enhanced chemical vapour deposition. However, due to the nature of the gases involved, (predominantly methane and hydrogen) the plasma is aggressive and chemically attacks many window materials including zinc sulphide and zinc selenide. This chemical attack

etches the surface of a zinc sulphide window and forms hydrogen sulphide. In order to protect the surface of the window material from attack a protective layer, called an interlayer, is employed. This interlayer may also promote diamond adhesion and provide stress relief. Deposition of a diamond layer occurs at high temperatures (between 500°C and 900°C), and during cooling of the coated window interface stresses between the diamond coating and window develop due to the large thermal expansion mismatch between the diamond coating and the IR window. An interlayer can be used to grade the stress to avoid interface failure and coating delamination. Metal oxynitrides such as zirconium oxynitride and hafnium oxynitride provide suitable interlayers for diamond deposition.

Figure 4 shows a representation of a coated window 40. The coated window 40 comprises a substrate 42 supporting a metal oxynitride layer 44 which in turn is coated with a diamond coating 46. In this embodiment the metal oxynitride layer is serving as a coating, a bonding layer and as an interlayer.

In commercial use it is anticipated that the coated window will also comprise an anti-reflection coating. This may be applied to the diamond coating 46 or directly to a metal oxynitride coating should the diamond coating not be present.

Metal oxynitride coatings provide hard and scratch resistant coatings for IR windows having a broad transmission range across IR and visible wavelengths. Additionally they can be used as bonding layer to support harder coatings or anti-reflection coatings as well as protective interlayers.

## Claims

1. A coating material (44) for a window (42) the coating material comprising metal oxynitride and being substantially transmissive to visible radiation and to IR radiation.
2. A coating material (44) according to claim 1 having the chemical formula  $M_{1-(y+z)}O_yN_z$  where M represents a metal element or combination of metals and y and z have values which vary depending upon the desired properties of the coating material.
3. A coating material (44) according to claim 2 characterised in that z is in the range 0.1 to 0.4.
4. A coating material (44) according to claim 2 or claim 3 characterised in that z is in the range 0.1 to 0.4.
5. A coating material (44) according to any of the preceding claims which comprises a bonding layer between the window (42) and another coating (46).
6. A coating material (44) according to any of the pre-

ceding claims which comprises a protective inter-layer (44) for protecting the window material (42) from further coatings (46) to be applied to the window.

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7. A coating material (44) according to any of the preceding claims which is deposited by dual beam ion sputtering.

8. A coating material (44) according to any preceding claim which is substantially transmissive to IR radiation in the region of 8 $\mu$ m. 10

9. A coating material (44) according to any preceding claim which is made by dual ion beam sputtering. 15

10. A method of producing a coating (44) of metal oxynitride on a sensor window (42) comprising the steps of:

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providing a sputtering target (10) containing the metal in a vacuum chamber (4);  
sputtering the target with a primary ion gun (16);  
bombarding a substrate (12) with ions of oxygen, nitrogen or both from a secondary ion gun (22); and  
depositing a coating of metal oxynitride on the substrate (12).

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11. A window (40) coated with a coating material (44) according to any preceding claim.

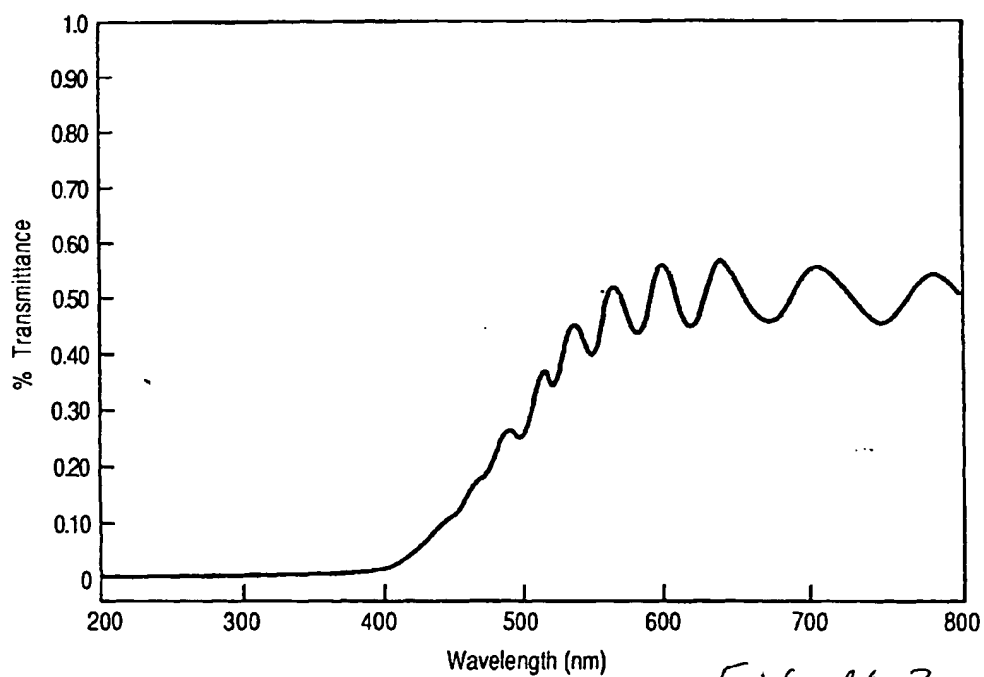
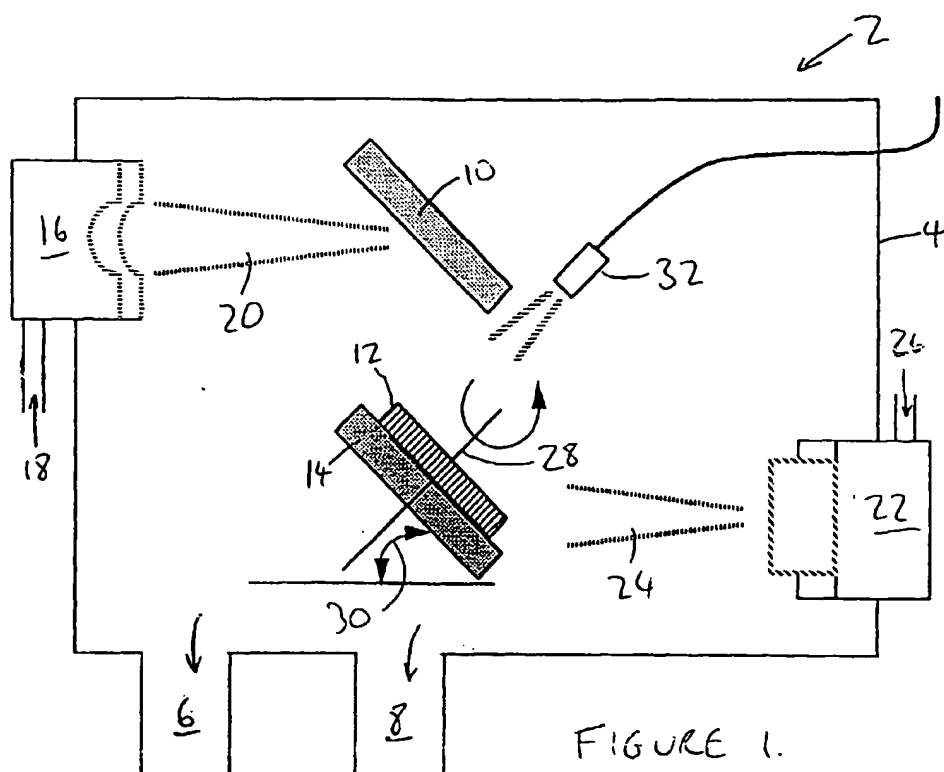
12. A sensor system comprising a sensor window (40) according to claim 11 and one or more radiation elements adapted to transmit or receive visible radiation, IR radiation or both. 35

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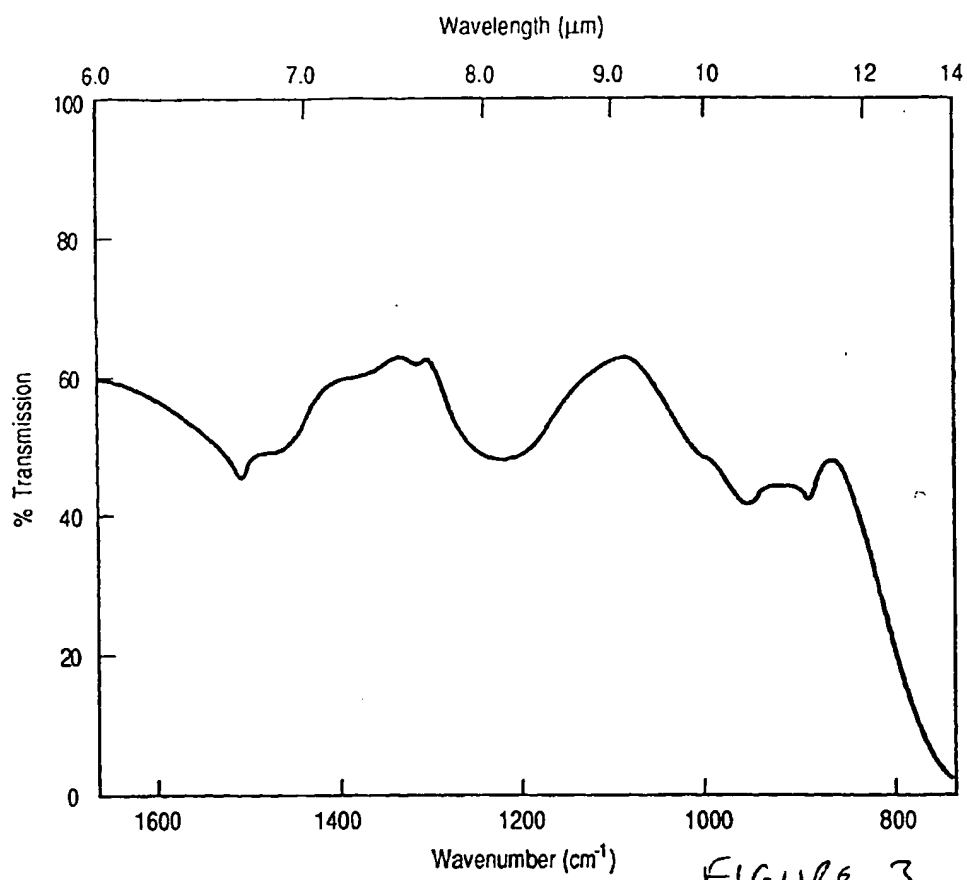


FIGURE 3.

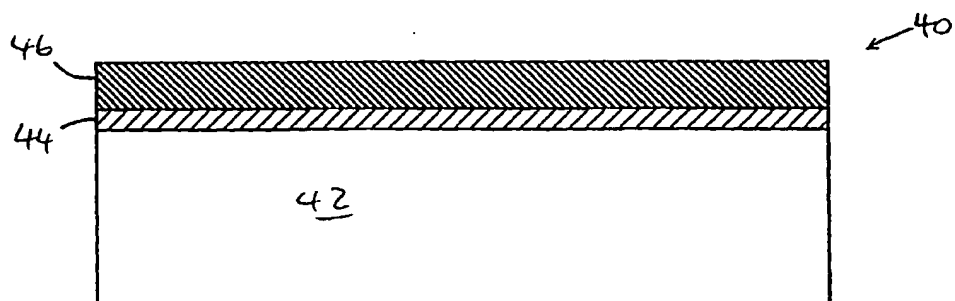


FIGURE 4.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 97 30 0908

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 5 085 926 A (IIDA YASUNOBU ET AL) 4 February 1992 * column 3, line 29 - column 8, line 48; figure 1; tables 1,2 *	1-11	G02B1/10
A	US 5 473 468 A (RUDIGIER HELMUT ET AL) 5 December 1995 * column 10, line 27 - column 18, line 24; figures 1-7,9 *	1-7,9-11	
D,A	GB 2 223 510 A (BARR & STROUD LTD ;LEWIS KEITH LODER (GB)) 11 April 1990 * page 3, line 25 - page 10, line 22; figures 1-5 *	1,5-12	
D,A	GB 2 082 562 A (SECR DEFENCE) 10 March 1982 * page 1, line 60 - page 2, line 6; figure 1 *	1,6-12	
A	EP 0 604 405 A (TERUMO CORP) 29 June 1994 * column 7, line 1 - column 11, line 16; figures 1-8 *	1,5,7-12	TECHNICAL FIELDS SEARCHED (Int.Cl.6)  G02B
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>20 May 1997</b>	Examiner <b>THEOPISTOU, P</b>
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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